Light-Scattering Study of Poly(hydroxy ester ether) in *N,N*-Dimethylacetamide Solution

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ABSTRACT: Static and dynamic light-scattering techniques were used to study biodegradable thermoplastic poly(hydroxy ester ether) in *N,N*-dimethylacetamide (DMAc). A weight-average molecular weight $M_W = 6.4 \times 10^4$ g/mol, radius of gyration $R_G = 9.4$ nm, second-virial coefficient $A_2 = 1.05 \times 10^{-3}$ mol mL/g^2, translational diffusion coefficient $D = 1.34 \times 10^{-7}$ cm^2/s, and hydrodynamic radius $R_H = 8.3$ nm are reported. In addition, the effect of H_2O on the polymer chain's conformation and architecture in a DMAc/H_2O solution is evaluated. Results suggest that H_2O makes the mixed solvent poorer as well as promotes polymer chain branching via intramolecular transesterification. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1737–1745, 2001

Key words: light scattering; poly(hydroxy ester ether); *N,N*-dimethylacetamide; mixed solvent; chain architecture

INTRODUCTION

Poly(hydroxy ester ethers) (PHEEs) are a group of hydroxy–functional polyesters synthesized by polymerizing diacids with stoichiometrically equivalent amounts of diglycidyl esters, catalyzed by quaternary ammonium halide.[1–3] High molecular weight, thermoplastic PHEEs can be conveniently prepared by this method. The polymer derived from the diglycidyl ether bisphenol A and adipic acid [HOOC—$(CH_2)_4$—COOH] is an amorphous material with a glass transition temperature, T_g, of 45°C. This thermoplastic biodegradable resin, referred to as PHEE, has good barrier and mechanical properties.[3]

In this study, light scattering (LS), both static and dynamic, was used to characterize this PHEE polymer in a *N,N*-dimethylacetamide (DMAc) solution. Parameters such as weight-average molecular weight M_W, radius of gyration R_G, second-virial coefficient A_2, translational diffusion coefficient D, and hydrodynamic radius R_H were measured. In addition, the effect of the presence of water, an effective plasticizer for the polymer, was also evaluated.

EXPERIMENTAL

Chemicals

PHEE resins (in pellet form) were provided by the Dow Chemical Co. (Midland, MI), synthesized as

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† Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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described in the literature. The solvent DMAc, HPLC grade, 99.9%, was purchased from Aldrich (Milwaukee, WI) and was used without any further purification. Reagent-grade water was obtained from a Barnstead (Dubuque, IA) Easypure UV/VF water-filtration system.

Solution Preparation

PHEE/DMAc stock solutions were prepared by dissolving PHEE resin in DMAc at room temperature under gentle magnetic stirring overnight. Subsequent dilutions were made by adding the solvent to the stock solution to make solutions of desired concentrations (mg/mL). Solutions of PHEE in a mixed solvent of DMAc + H_2O were made by mixing DMAc and H_2O to achieve the desired H_2O content (percent by volume) in the mixed solvent, then by following the general procedure as described above to prepare stock solutions and the subsequent dilutions. Solutions for LS experiments were filtered through Whatman (Clifton, NJ) disposable syringe filters (PTFE filter media with polypropylene housing, 25-mm diameter, 0.2-μm pore size) into acetone-rinsed and dried scintillation vials (SVs) for measurement. The samples were allowed to stand for 2 weeks prior to LS measurements.

Specific Refractive Index Increment (*dn/dc*)

This parameter was measured using a Chromatix™ KMX-16 laser differential refractometer, with a He—Ne laser (λ = 632.8 nm) as a light source. The refractometer was calibrated with aqueous NaCl solutions of seven different concentrations, ranging from 0.5 to 2 g NaCl/100 g H_2O. The measurements were made at 25°C.

The determination of the differential refractive index is accomplished by measuring the deviation of the He—Ne laser beam passing through a divided cell composed of adjacent solvent and solution compartments. The beam deviation is proportional to the difference in the refractive index (Δn) between the polymer solution and the respective solvent. To calculate Δn, the beam deviation is multiplied by a calibration constant, determined from the calibration procedure with $NaCl_{(aq)}$ as described above. In this study, polymer solutions of five different concentrations, ranging from 2 to 10 mg/mL, were used for the Δn measurements. The slope of the linear least-squares fitting of Δn versus c yielded dn/dc.

Static Light Scattering (SLS)

A DAWN-DSP laser photometer (Wyatt Technology Corp., WTC, Santa Barbara, CA) was used off-line to determine the M_W, R_G, and A_2 of the PHEE/DMAc systems. The LS signals were detected simultaneously at 18 scattering angles, θ, ranging from 22.5° to 147°. A He—Ne laser with λ = 632.8 nm was used as the light source. The apparatus was operated in the batch mode, using an SV as the scattering cell. All measurements were made at 25.0 ± 0.2°C. The operation software was ASTRA™ 4.7 for Windows™, provided by WTC. The same software was also used for data analysis. The photometer was calibrated with toluene filtered through a 0.02-μm filter (Whatman Anotop™) and normalized with a 10 mg/mL polystyrene/toluene solution (M_W = 4000, M_W/M_N = 1.04).

The basis for SLS data analysis is the following equation[4]:

$$\frac{R_\theta}{Kc} = M_W P(\theta) - 2A_2 c M_W^2 P^2(\theta) \qquad (1)$$

The excess Rayleigh ratio, $R(\theta)$, depends on the intensity of the scattered light $I(\theta)$. K is an optical constant, $K = 4\pi^2 n^2 (dn/dc)^2 \lambda^{-4} N_A{}^{-1}$, where n is the refractive index of the solvent; λ, the wavelength of the incident beam; dn/dc, the specific refractive index increment of the polymer/solvent system; and N_A, Avogadro's number. $P(\theta)$ is the form factor which depends on the polymer size (R_G), shape, and structure:

$$P(\theta) = 1 - \frac{(R_G^2 q^2)}{3} + O(q^4), \qquad (2)$$

where $q = (4\pi n/\lambda)\sin(\theta/2)$‡ is the scattering vector.

From the limits of $R(\theta)$ as $\theta \to 0$, $c \to 0$, parameters M_W, R_G, and A_2 can be obtained. This can be achieved by either the Zimm plot of $Kc/R(\theta)$ versus $\sin^2(\theta/2)$ or with the Berry plot of $[Kc/R(\theta)]^{1/2}$ versus $\sin^2(\theta/2)$. In this study, the Berry method was used throughout the analysis, since, in some of our cases, the Zimm plot gave erroneous results such as negative R_G values. The SLS

‡ The refractive index for a mixed solvent, n_{ms}, was calculated using the Lorenz–Lorentz equation,[5] $(n_{ms}^2 - 1)/(n_{ms}^2 + 2) = \phi_1 [(n_1^2 - 1)/(n_1^2 + 2)] + \phi_2 [(n_2^2 - 1)/(n_2^2 + 2)]$, where ϕ_1, ϕ_2, and n_1, n_2 are the volume fractions and refractive indexes of solvent 1 and solvent 2, respectively.

apparatus, the operation system, and the data analysis were verified by measuring a polystyrene molecular weight standard with a narrow distribution (Polysciences, Inc., Warrington, PA, M_W = 400,000, M_W/M_N = 1.06) in toluene and comparing the measured values with the values supplied by the manufacturer and the values reported in the literature. The results proved to be satisfactory: M_W (measured) = 4.08 ± 0.08 × 10^5 g/mol.

Dynamic Light Scattering (DLS)

DLS measurements were performed with a Brookhaven Instruments Corp. (BIC, Holtsville, NY) BI-9000AT autocorrelator and a variable-scattering angle BIC BI-200SM goniometer with a stepping motor controller, using the λ = 514.5-nm line of an argon laser (Lexel Laser, Inc., Fremont, CA) to illuminate the sample cell, an SV. The sample cell was placed in a thermostatted glass vat with an optically flat window, filled with *cis–trans*-decahydronaphthalene (trade name Decalin) as the index matching liquid to match the refractive index of the SV and the vat. All experiments were carried out at 25.0 ± 0.1°C. The scattered intensity at the scattering angle θ, $I(\theta)$, was determined using standard photon counting methods. With this instrument, it was possible to cover an angular range of θ = 30°–150°, which corresponds to a range of 0.9–3 × 10^7 m^{-1} for the scattering vector q. Intensity autocorrelation functions, $G_2(t)$, covering the decay of the intensity fluctuations over six decades of time were measured.

The decay of $G_2(t)$ provides a measure of the diffusion coefficient D of the macromolecules in the solution.[6] If there is only one size of the macromolecule in a dilute solution, then

$$G_2(t) = B + A \exp(-2\Gamma t), \tag{3}$$

where A denotes the dynamic amplitude, and B, the baseline of the measured correlation function (related to the total intensity scattered at the scattering vector q). Γ is the decay rate. For the motion of particles in solution that is purely diffusive, Γ is related to the diffusion coefficient D via the following equation:

$$\Gamma = Dq^2 \tag{4}$$

The hydrodynamic radius R_H of the macromolecule can then be derived from D by using the Stokes–Einstein equation:

$$R_H = \frac{k_B T}{6\pi\eta D} \tag{5}$$

where k_B is the Boltzmann constant; T, the absolute temperature; and η, the viscosity of the solvent.#

In a polydisperse solution, there may be many different species, each diffusing with its own characteristic diffusion coefficient. In this case, it is possible to obtain the distribution $A(D)$ of species with the diffusion coefficient D from the normalized electric field autocorrelation function, $g_1(t)$:

$$g_1(t) = \left[\frac{(G_2(t) - B)}{A}\right]^{1/2} \tag{6}$$

$$g_1(t) = \int A(D)\exp(-Dq^2t)dD \tag{7}$$

The determination of $A(D)$ from eq. (7) can be realized by Laplace inversion techniques. In this study, $A(D)$ was obtained from the measured correlation functions by using the REPES program which employs the Laplace inversion.[7–10]

The alignment of the DLS system was checked by measuring the $I(\theta)$ of filtered toluene in the range of θ = 15°–155°, then plotting $I(\theta)\sin(\theta)$ versus θ. The alignment proved to be satisfactory: % error [of $I(\theta)\sin(\theta)$ normalized to average] ≤ 1.3%. The operation of the system and the data analysis were verified by measuring the size of the polystyrene nanospheres suspended in water and then comparing the calculated R_H value to that provided by the manufacturer. The agreement was good: R_H (manufacturer) = 48 ± 1.6 nm; R_H (measured) = 48.2 ± 0.3 nm.

RESULTS AND DISCUSSION

Specific Refractive Index Increment *dn/dc* Measurements

The dn/dc value was measured using a series of PHEE solutions in the concentration range $2 < c < 10$ mg/mL. At least eight readings were taken at each concentration, and a standard deviation

The viscosity for the mixed solvent, η_{ms}, is calculated based on the following equation: $\eta_{ms} = \phi_1\eta_1 + \phi_2\eta_2$, where η_1 and η_2 are the viscosities of solvent 1 and solvent 2, respectively.

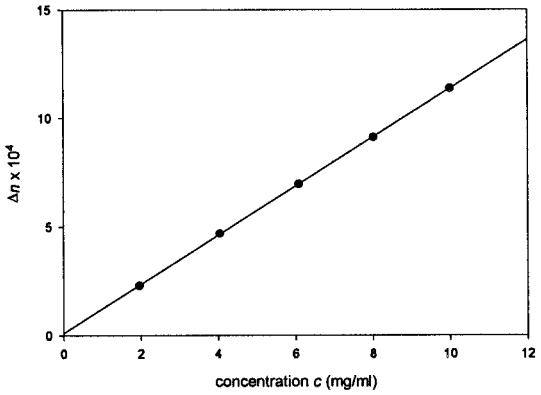

Figure 1 Determination of the specific refractive index increment *dn*/*dc* for PHEE/DMAc at 25°C. The error bars for the data points were smaller than the size of the symbols used. The standard deviation for *dn*/*dc*: *dn*/*dc* = 0.113 ± 0.0003 mL/g, was obtained by linear least-squares fitting of the data.

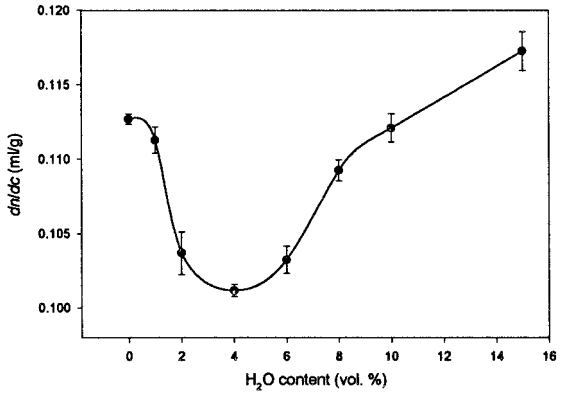

Figure 2 *dn*/*dc* values of PHEE with different H_2O contents. Each *dn*/*dc* value and its standard deviation were determined as described in the text and in Figure 1. The curve is drawn to guide the eye.

was calculated based on the mean value of these readings. A Δn value for each concentration was then obtained from the mean value of the readings for the concentration and the calibration constant of the apparatus, determined as described in the Experimental section. Figure 1 shows the result of Δn versus c measurements for the PHEE/DMAc solutions. The straight line shows the least-squares fitting. The slope of the fitting gives *dn*/*dc*. The value, *dn*/*dc* = 0.113 ± 0.0003 mL/g, was obtained for PHEE/DMAc at 25°C. This *dn*/*dc* value is in the typical range for polymer solutions.[4]

Effect of Solvent on *dn/dc*

The H_2O content of the solution had a peculiar effect on the *dn*/*dc* value, as shown in Figure 2. Investigation on PHEE solutions of DMAc with different H_2O content showed that *dn*/*dc* decreases as the H_2O content increases from 0 to 4%, reaches a minimum at ~4% H_2O content, then increases as the H_2O content increases. It is speculated that there is certain degree of complex formation between PHEE and DMAc. The addition of H_2O breaks down this complex structure. At 4% H_2O content, the complex structure is completely destroyed. The *dn*/*dc* value then increases monotonically with the increasing H_2O content beyond 4% H_2O, since the refractive index of H_2O is smaller than that of DMAc: $n_{H2O} = 1.333$ versus $n_{DMAc} = 1.438$.

SLS Measurements

SLS measurements were carried out on the WTC DAWN-DSP photometer; all measurements were made at 25.0 ± 0.2°C. The Berry plot, based on eq. (1), was used for data analysis. The *dn*/*dc* values used in the calculation were measured as described above. In general, five concentrations ranging from 2 to 10 mg/mL were used, and scattering intensities at 18 scattering angles were collected and used in the calculation. Values at low θ were less certain in some cases, as expected. However, the calculation results were not significantly changed if the scattering values at low θ were eliminated from the data analysis. To be consistent, all scattering angles were used in the calculation throughout the data analysis for different systems.

Figure 3 shows the Berry plot for the PHEE/

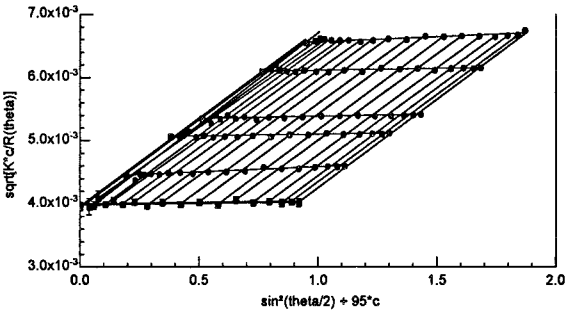

Figure 3 Berry plot for PHEE in DMAc. Concentrations of the five solutions: $c1$ = 2.03 mg/mL; $c2$ = 4.01 mg/mL; $c3$ = 5.39 mg/mL; $c4$ = 8.04 mg/mL; $c5$ = 10.00 mg/mL. The range of the scattering angles measured was 22.5°–147°.

Table I Molecular Parameters of PHEE in DMAc with Different H_2O Contents, Measured by SLS at 25°C

H_2O Content (vol %)	$M_W \times 10^{-4}$ (g/mol)	R_G (nm)	$A_2 \times 10^4$ (mol mL g^{-2})
0	6.4 ± 0.09	9.4 ± 3.8	10.46 ± 0.36
1.0	6.4 ± 0.05	16.7 ± 1.1	9.68 ± 0.16
2.0	7.3 ± 0.08	15.4 ± 2.0	8.40 ± 0.21
4.0	7.4 ± 0.09	17.8 ± 1.9	7.27 ± 0.21
6.0	7.6 ± 0.07	22.0 ± 1.3	7.00 ± 0.16
8.0	6.4 ± 0.03	14.6 ± 1.1	6.67 ± 0.12
10.0	6.2 ± 0.08	18.3 ± 1.6	5.51 ± 0.27

DMAc solution. The results are $M_W = 6.4 \pm 0.09 \times 10^4$ g/mol, $R_G = 9.4 \pm 3.8$ nm, and $A_2 = 1.05 \pm 0.036 \times 10^{-3}$ mol mL g^{-2}. Within experimental error, the M_W value obtained here is identical to that measured by gel permeation chromatography (GPC) at Dow Chemical: $M_W = 6.5 \times 10^4$ g/mol.‖ The large, positive value of A_2 indicates that DMAc is a good solvent for PHEE at 25°C. The relatively large uncertainty of R_G (~40%) is probably due to the fact that the size of the macromolecule measured is at the lower limit of the instrument (~10 nm). However, it is necessary to point out here that the ASTRA software package (by WTC) offers different polynomial degrees for concentration and angle fits of the scattering data. The fitting results, R_G values in particular, are dependent on the fitting degrees used. (For example, $R_G = 27.6 \pm 3.5$ nm is obtained when the first-degree angle fit and second-degree concentration fit are used in the Berry plot to analyze the same set of data as shown in Fig. 3.) To be consistent, first-degree concentration and angle fits were used in the Berry plot for all SLS data analysis.

Table I summarizes the measured SLS results for PHEE in DMAc with different H_2O contents. Of the three parameters measured, M_W seems to have two different groups of values: $M_W \sim 6.4 \times 10^4$ g/mol at H_2O contents of 0, 1.0, 8.0, and 10.0%, and $M_W \sim 7.4 \times 10^4$ g/mol at H_2O contents of 2.0, 4.0, and 6.0%. The reason for this variation is not clear to us at this point. The R_G values, except for two solutions at H_2O contents of 0 and 6.0%, remained relatively unchanged, with a mean value at ~17 nm. Only A_2 had a definitive trend with the change in H_2O content. It decreased monotonically as the H_2O content increased, from 1.05×10^{-3} at 0% H_2O content to 5.5×10^{-4} mol mL g^{-2} at 10.0% H_2O content, a 50% decrease. This clearly indicates that the addition of H_2O to DMAc makes it a poorer solvent for the polymer.[11]

‖ Dow Chemical Application Note.

Overlap Concentration

The transition from dilute to semidilute for a polymer solution occurs at a concentration designated as c^*, at which point the macromolecules will fill the available volume. de Gennes[12] introduced the concept of "overlap concentration" for c^*, since, in the semidilute region, the individual chains overlap to form many contacts and become entangled. For dilute solutions, $c < c^*$, the macromolecules are so far apart from each other that any interactions between macromolecules are virtually negligible and have little impact on any physical properties of the solution. For semidilute solutions at $c > c^*$, a drastic change in the solution properties is expected and generally observed. The value of c^* depends on factors such as the definition of a polymer chain's dimension and conformation. For flexible linear chains, the following conventions are often used[13]:

$$c^*_{R_G} = \frac{M_W/N_A}{\frac{4\pi}{3} R_G^3} \tag{8}$$

$$c^*_{R_H} = \frac{M_W/N_A}{\frac{4\pi}{3} R_H^3} \tag{9}$$

$$c^*_{A_2} = (A_2 M_W)^{-1} \tag{10}$$

Using the average values from SLS measurements for the PHEE solutions, $M_W = 6.8 \times 10^4$ g/mol, $R_G = 16.3$ nm, $A_2 = 1.05 \times 10^{-3}$ mol mL g^{-2} (PHEE/DMAc), and $R_H = 10.1$ nm (see the following section), c^* was calculated from eqs. (8), (9), and (10): $c^*_{R_G} = 6$ mg/mL, $c^*_{R_H} = 26$ mg/mL, and $c^*_{A_2} = 14$ mg/mL.

The differences among $c^*_{R_G}$, $c^*_{R_H}$, and $c^*_{A_2}$ values are not surprising. Since c^* cannot be uniquely defined, various c^* definitions can differ in value by a factor of up to 10. Here, c^* is only used as a guideline to determine the borderline between dilute and semidilute regions. The highest con-

centration used here was 10 mg/mL; the lowest was 2 mg/mL, and the experimental results were extrapolated to $c \rightarrow 0$ to obtain parameters such as M_W, R, etc. Therefore, it is safe to assume that the solutions studied here are dilute solutions; it is also valid to use the well-established theoretical procedures for the dilute region for data interpretation, and the results obtained reflect the physical properties of the macromolecules.

DLS Measurements

The same samples used in the SLS studies were used for the DLS measurements. Figure 4(A) shows an example of the experimentally measured autocorrelation function for PHEE/DMAc. The distribution $A(D)$ versus D is calculated by the REPES program according to eqs. (6) and (7). R_H is then obtained via eq. (5), and the resulting distribution profile of $A(R_H)$ versus R_H is shown in Figure 4(B). It is evident that the autocorrelation function in Figure 4(A) does not show distinguishably different diffusion modes. This is also demonstrated by the Laplace inversion of the correlation function: the resulting distribution [as shown in Figure 4(b)] shows a broad singular distribution with no apparent aggregates present. This indicates that the PHEE polymer used in this study has a broad molecular weight distribution, which is in good agreement with the manufacturer's GPC measurements.§

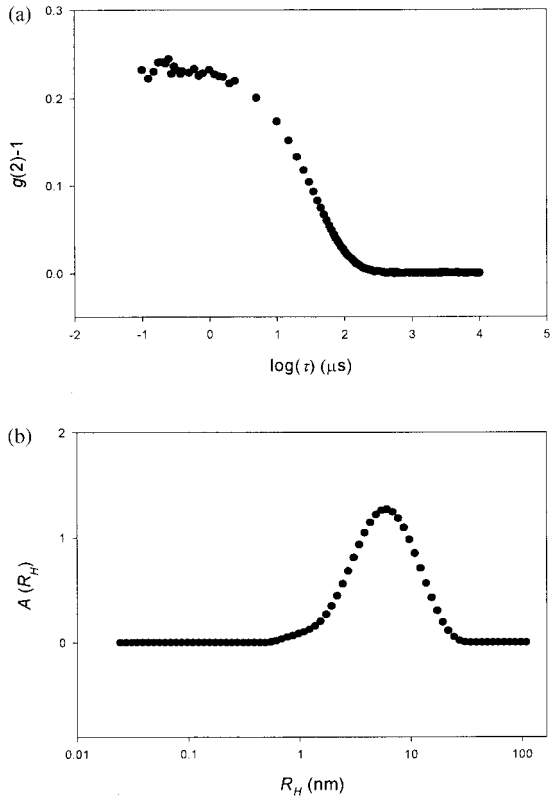

Figure 4 (a) Intensity autocorrelation function for PHEE/DMAc, c = 2.0 mg/mL, measured by DLS at θ = 90°, 25°C. (b) Distribution of hydrodynamic radius R_H obtained by the REPES analysis from the correlation function shown in (a).

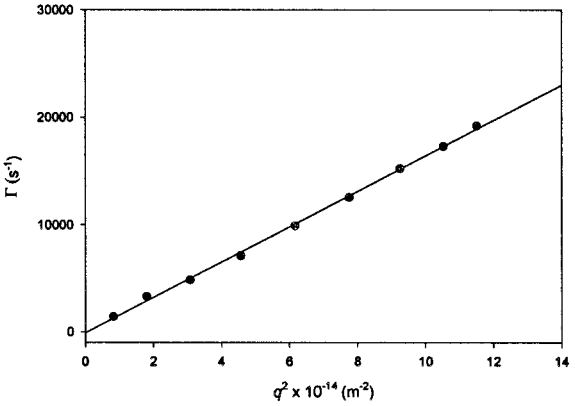

Figure 5 The q-dependence of the decay rate, Γ, obtained by the REPES analysis for PHEE in DMAc. The straight line represents a least-squares fitting, and the slope of the fitting gives the diffusion coefficient D.

DLS measurements for each solution were made in the θ range of 30°–150°, at 15° increments. The value of the decay rate $\Gamma_{(\theta)}$, which represents the average value of the broad singular distribution, was then obtained through eqs. (3), (4), (6), and (7). Figure 5 shows as an example the q-dependence of $\Gamma_{(\theta)}$ for PHEE in DMAc. The excellent linear relationship between $\Gamma_{(\theta)}$ and q^2 implies that the motion is indeed purely diffusive. The diffusion coefficient D is then obtained as the slope of the $\Gamma_{(\theta)}$ versus q^2 fit. Subsequently, the D value for each solution was obtained by this method.

As in SLS, for each PHEE/DMAc + H_2O system, five different concentrations ranging from 2 to 10 mg/mL were used in the DLS measurements, and Figure 6 shows the typical concentration dependence of D. It is evident that D increases as c increases. It is known that[14]

$$D_{(c)} \sim D_0(1 + k_d c) \tag{11}$$

$$k_d = 2A_2M_W - \frac{C_D N_A R_H^3}{M_W} \tag{12}$$

§ Dow Chemical Application Note.

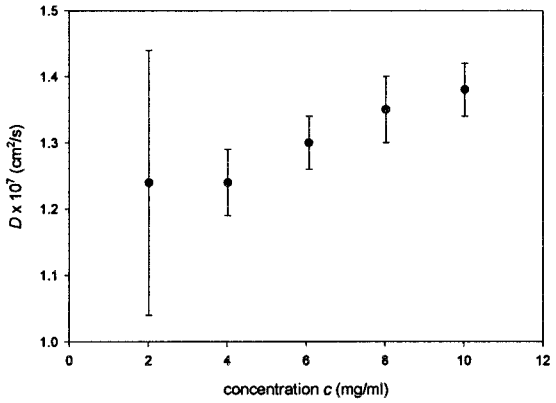

Figure 6 Concentration dependence of diffusion coefficient D. The D value and the error bar at each concentration were determined as described in the text and in Figure 5. Solution used: PHEE in DMAc with 4.0% H_2O content. 25°C.

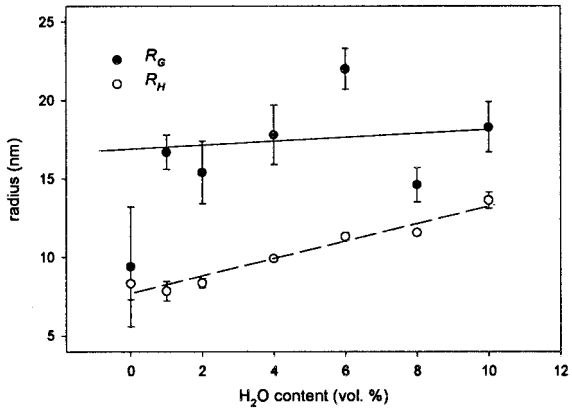

Figure 7 Hydrodynamic radius R_H and radius of gyration R_G of PHEE in DMAc at different H_2O contents. The lines were drawn to guide the eye; the first R_G point was not included in drawing the line because of its large uncertainty. The numerical values of R_H and R_G can be found in Tables I and II.

where D_0 is the diffusion coefficient at $c \rightarrow 0$ and C_D is a positive constant. A linear fitting of $D(c)$ versus c according to eq. (11) would yield D_0 and k_d values. Table II shows the fitting results.

The monotonic decrease of k_d with increasing H_2O content can be explained by eq. (12). It is known from SLS studies, as described in the previous section and in Table I, that A_2 decreases with increasing H_2O content and M_W remains relatively unchanged. Therefore, the thermodynamic term ($2A_2M_W$) for k_d decreases with increasing H_2O content. The hydrodynamic term ($C_DN_AR_H^3/M_W$) increases with increasing H_2O content, because of increasing R_H (decreasing D_0, as shown in Table II). The combined result is that k_d decreases with increasing H_2O content. As a matter of fact, there are studies using the k_d values to estimate the Flory Θ-temperature and Θ-solvent.[15] This condition did not materialize in this study, however, because the lowest A_2 at 10.0% H_2O content is still 5.5×10^{-4} mol mL g^{-2}, close but not yet to 0, suggesting that this particular mixed solvent at 25°C has not quite yet reached the Θ-conditions.

Figure 7 shows the hydrodynamic radius R_H, as determined from the diffusion coefficient D_0 via eq. (5) of PHEE in DMAc with different H_2O contents, as well as R_G. The increase of R_H with increasing H_2O content is apparent, while R_G remains relatively unchanged. Figure 8 shows the distribution profiles of PHEE in DMAc with four different H_2O contents. The shape of the distribution does not change significantly as the H_2O content changes. Instead, the whole distribution shifts toward larger R_H as the H_2O content increases. In other words, the increase in R_H is not caused by the formation of some distinguishably larger aggregates, because no separate slow

Table II Dynamic Parameters Obtained by DLS on PHEE in DMAc with Different H_2O Contents According to Eq. (11)

H_2O Content (vol %)	$D_0 \times 10^7$ (cm^2/s)	$k_d \times 10^2$ (mL/mg)	R_H (nm)	ρ (R_G/R_H)
0	1.34 ± 0.17	6.3 ± 2.3	8.3 ± 1.0	1.13 ± 0.68
1.0	1.43 ± 0.11	4.6 ± 1.7	7.8 ± 0.6	2.13 ± 0.34
2.0	1.35 ± 0.05	2.2 ± 0.7	8.4 ± 0.3	1.84 ± 0.31
4.0	1.15 ± 0.02	1.9 ± 0.3	9.9 ± 0.1	1.79 ± 0.22
6.0	1.02 ± 0.02	1.9 ± 0.4	11.3 ± 0.2	1.94 ± 0.16
8.0	1.01 ± 0.02	1.0 ± 0.3	11.6 ± 0.001	1.26 ± 0.10
10.0	0.867 ± 0.033	0.92 ± 0.5	13.6 ± 0.5	1.34 ± 0.18

D_0 is the intercept at $c \rightarrow 0$ of the linear least-squares fitting and k_d is the slope. R_H is calculated from D_0 according to eq. (5).

modes representing large aggregates were seen in the distribution profile.

The notion that no large aggregates were formed with the addition of H_2O was further supported by the SLS results, which demonstrated that M_W and R_G remain relatively unchanged with increasing H_2O content, as described in the previous section. The question that has to be answered here is why R_H increases while R_G and M_W remain unchanged. There are principally two possibilities: (I) a change in PHEE's polydispersity and/or (II) a change of the polymer chain conformation and/or architecture. Figure 8 shows that the distribution profile does not change drastically with the addition of H_2O; therefore, polymer polydispersity does not play a major role here. A parameter that has strong chain conformation/architecture dependence is the so-called ρ parameter that can be obtained from a combination of dimensions measured by SLS and DLS, that is, R_G and R_H: $\rho = R_G/R_H$. The ρ parameter has been calculated for different chain conformation, architecture, and polydispersity[16]: $\rho > 2$ for a rigid rod, $\rho \sim 2$ for a polydisperse random coil in a good solvent and decreases to $\rho \sim 1.7$ in Θ-solvent, $\rho \sim 1.0$–1.3 for branched chains under Θ-conditions, and $\rho \sim 0.78$ for uniform spheres. The ρ parameters for PHEE in DMAc with different H_2O contents are listed in Table II.

Except for the system of PHEE in pure DMAc where the R_G value is somewhat problematic (~40% uncertainty), as discussed in the previous section, ρ for PHEE in DMAc decreases as the H_2O content increases, as shown in Figure 9. At low H_2O contents (1.0–6.0%), $\rho > 1.7$, indicating

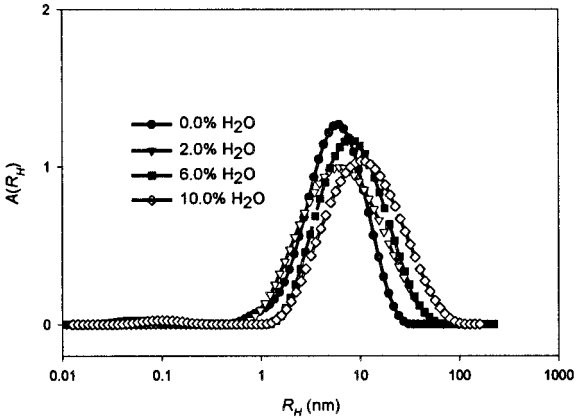

Figure 8 Distribution profiles of R_H for PHEE in DMAc with different H_2O contents, determined as described in the text and Figure 4.

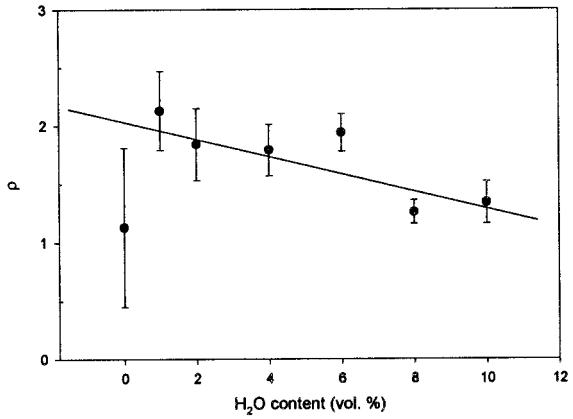

Figure 9 ρ (R_G/R_H) of PHEE in DMAc at different H_2O contents. The line is drawn to show that ρ decreases with increasing H_2O content. The first ρ point was not included in drawing the line because of its large uncertainty. The numerical values of ρ can be found in Table II.

that the solvent is indeed a good solvent, and PHEE assumes an expanded random coil conformation in the solution. As the H_2O content increases, the solvent becomes poorer, and at 8–10% H_2O contents, the system has a ρ parameter equivalent to a star polymer ($f = 4$, f = number of rays per star, functionality of the star center, $f = 1$ for linear polymer) under Θ-conditions, for example, $\rho = 1.3$. In other words, the addition of H_2O to the PHEE/DMAc system does two things: (I) it makes the solvent poorer for the polymer, and (II) at H_2O contents ≥8.0%, it causes the polymer to undergo a structural rearrangement to assume an architecture similar to a star polymer. Because M_W as measured by SLS does not change, the structural rearrangement must be predominantly intramolecular in nature. Since PHEE has a tendency to participate in an intramolecular transesterification reaction,[2] it is therefore speculated that the addition of H_2O promotes this intramolecular transesterification, thus producing branched polymer chains while M_W values and the distribution profiles remain unchanged. The dense packing of branched chains prevents more and more the draining of the solvent; therefore, R_H increases strongly as the degree of branching increases while R_G remains relatively unchanged—hence, the decrease of ρ.

CONCLUSIONS

SLS and DLS were used to characterize PHEE in DMAc and to study the effect of H_2O on the sys-

tem. The results showed that DMAc at 25°C is a good solvent for the polymer, and the addition of H_2O makes the mixed solvent poorer. Moreover, the results showed that M_W, R_G, and the distribution profile of the polymer remain unchanged, while R_H values increase with increasing H_2O content. That H_2O promotes PHEE's intramolecular structural rearrangement is the mechanism proposed to explain the above observations.

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